

# **Biomass to Hydrogen via Pyrolysis and Reforming**

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## **Abstract**

Pyrolysis of lignocellulosic biomass and reforming of the pyrolygneous oils is being studied as a strategy for the production of hydrogen. New technologies for the rapid pyrolysis of biomass have been developed in the past decade. They provide compact and efficient systems to transform biomass into vapors which are condensed to oils, with yields as high as 75-80% by weight of the anhydrous biomass. This "biocrude" is a mixture of aldehydes, alcohols, acids, oligomers from the constitutive carbohydrates and lignin, and some water produced during the dehydration reactions. Hydrogen can be produced by reforming the biocrude with steam. A process of this nature has the potential to be cost competitive with conventional means of hydrogen production.

The concept of hydrogen from biomass offers significant opportunities for novel research and development. The use of a renewable resource feedstock is an alternative to conventional means of hydrogen production from petroleum and natural gas. As a consequence, the environmental benefit of zero net carbon dioxide emissions facilitates the approach to a pollution-free energy system. An additional benefit is that a regionalized system of hydrogen production can be envisioned using this technology. Small and medium-sized pyrolysis units (<500 Mg/day) could provide the biocrude to a centralized reforming facility to be catalytically converted to the  $H_2$  and  $CO_2$ . Therefore, storage and transportation problems associated with hydrogen production become less important in the economics of the process. The reforming facility can be designed to handle alternate feedstocks, such as natural gas and naphtha, if necessary. Additionally, the biocrude can first be refined to yield valuable oxygenates so that only the residue is used for hydrogen production.

Project work is being conducted in five areas: literature reviews on the composition of pyrolysis oils and the technology of steam reforming to hydrogen; thermodynamic modelling to guide experimental design;

experimental research and catalyst testing; process development; economic evaluation; and environmental impact studies. Thermodynamic modelling of the major constituents of the biocrude has shown that reforming is possible within a wide range of steam/compound ratios. Additionally, catalytic reforming of model compounds to hydrogen using a Ni-based catalyst has begun. Existing catalytic data on the reforming of oxygenates has been studied to guide catalyst selection. An initial process diagram for the pyrolysis and reforming operations will also be presented, along with initial production cost estimates.

## Introduction

Gasification of solid fuels to yield syngas (a mixture of  $H_2$  and  $CO$ ), followed by shift conversion to produce  $H_2$  and  $CO_2$ , and steam reforming of hydrocarbons are well established processes. Renewable lignocellulosic biomass has been considered as a potential solid fuel feedstock for gasification. Economics of current processes favor the use of hydrocarbons (natural gas,  $C_2$ - $C_5$ , and naphtha) and inexpensive coal as feedstocks. An alternative approach to  $H_2$  production begins with fast pyrolysis of biomass.

Recent advances in the understanding of pyrolytic mechanisms and in the technology needed to achieve high heat transfer rates to particles, while controlling secondary cracking reactions responsible for gas and char production, have led to the development of fast pyrolysis routes. These convert biomass materials in high yields (~ 75% wt of dry biomass) into a "pyrolytic oil," or "biocrude." Typically, 85% wt of the biocrude is made of oxygenated organic compounds (Elliott, 1988): acids, alcohols, aldehydes, ketones, furans, substituted phenolics and complex oxygenates derived from biomass carbohydrates and lignin. About 15% wt of the biocrude is water from the dehydration reactions. Very little ash and char are present in the biocrude when appropriate filtration technology is used in the pyrolysis process.

Results from fluid bed fast pyrolysis (Radlein et al., 1991) have shown that a 76% wt yield of biocrude can be obtained from poplar ( $CH_{1.47}O_{0.67}$ ). The organic fraction of the biocrude represents 85% wt and its elemental composition is  $CH_{1.33}O_{0.53}$ . Table 1 shows the expected yields of hydrogen from two thermochemical routes (pyrolysis and gasification), compared to the theoretical yield of the reaction between wood and steam using externally supplied heat.

Table 1. Comparison of  $H_2$  yields from biomass process routes

Process Routes	Yield of Hydrogen (% wt biomass)	<u>Energy Content (HHV) of <math>H_2</math></u> Energy Content of Biomass
Pyrolysis + Catalytic Reforming	12.6	91%
Gasification + Shift Conversion	11.5	83%
Biomass + Steam + External Heat (Theoretical Maximum)	17.1	124%

Calculations were made using current yields for non-optimized fast pyrolysis (Radlein et al, 1991) and gasification (Probstein and Hicks, 1982) processes. The  $H_2$  production potential for these two routes is similar. However, the pyrolysis process is less severe and does not require an oxygen supply as in gasification. Both options require steam for the reforming and shift conversion steps.

The objectives of our investigation are:

- To determine via thermodynamic simulations the conditions under which the components of the pyrolytic oils can be steam reformed to  $H_2$  and  $CO_2$ , including equilibrium yields as a function of steam to carbon ratio and temperature
- To assess the scientific feasibility of catalytically converting the oxygen-rich pyrolytic oil compounds and to select suitable catalysts and conditions to be used

- To conduct an experimental bench scale program to determine real yields as a function of treatment severity, catalyst type and experimental conditions
- To develop a process flow diagram based on the results obtained and conduct economic calculations as a function of plant capacity.

### **Fast Pyrolysis: Biocrude Yields and Composition**

Three technologies appear to be capable of achieving high yields of biocrude by a proper combination of temperature, time and heat transfer rates.

- Fluid beds (Piskorz et al, 1988): 450°C-550°C, < 0.5s
- Entrained beds (Graham and Freel, 1988): ~650°C, < 1.0s
- Ablative reactors, i.e. vortex (Diebold and Scahill, 1988): 450°C-625°C, < 1.0s

In the above technologies, 55-70% wt of mf biomass is the organic fraction of the biocrude, and 5-15% wt is water. A fourth technology (Roy et al, 1990), vacuum pyrolysis, has also demonstrated the ability to produce high biocrude yields. From this process, the organic fraction represents 50-60% wt of mf biomass and water 13-16% wt. Reliable values of oil, water, char and gas yields are difficult to obtain because of unclosed and/or unreported material balances. The composition of typical oils has only been reported in quantitative detail by the University of Waterloo, Canada (Piskorz et al, 1988), and is shown in Table 2.

**Table 2: Pyrolytic Oil Composition Derived from Poplar (Radlein et al, 1991)**

<u>Yields</u>	<u>wt % mf wood</u>
Oil*	65.8
Water*	12.2
Char	7.7
Gas	10.8
Unaccounted	3.5
 <u>Composition</u>	
Acetic Acid	5.4
Formic Acid	3.1
Hydroxyacetaldehyde	10.0
Glyoxal	2.2
Methylglyoxal	0.65
Formaldehyde	1.2
Acetol	1.4
Ethylene Glycol	1.05
Levogluconan	3.0
1,6-Anhydroglucofuranose	2.4
Fructose (?)	1.3
Glucose	0.4
Cellobiosan	1.3
Oligosaccharides	0.7
Pyrolytic Lignin**	16.2
Unidentified	15.5

\*Oil + Water = Biocrude

\*\*Material precipitated by addition of water

Variations in the composition of pyrolysis oil as shown in Table 2, should be expected as a function of raw material, pyrolysis treatment severity (T, t, and dT/dt profiles) and the use of catalysts during the pyrolytic step. However, the information presented in Table 2 clearly indicates that the biocrude is essentially a mixture of two major acids (acetic and formic), aldehydes and alcohols plus a significant fraction of lignin (denoted as pyrolytic lignin), probably present as a low to medium molecular weight material since it precipitates by simple addition of water. Based on the mechanistic works of Antal (1982), Shafizadeh (1982), and Richards (1987), the unidentified compounds should contain a large number of carbohydrate-derived components. Monomeric lignin-derived products having alcohol characteristics should also be present (Elliott, 1988).

The oxygenated biocrude may be an appropriate feedstock for further catalytic steam reforming to H<sub>2</sub> and CO<sub>2</sub> using a conversion strategy paralleling that of catalytic steam reforming of alcohols. Optimization of the pyrolysis conditions to obtain high yields of biocrude having a significant fraction of low molecular weight aldehydes and alcohols is required.

## Thermodynamics

Thermodynamic simulations of the reforming reaction were performed in order to guide experimental design and determine equilibrium constraints. These simulations were performed on ASPEN Plus using compounds representative of the oil and a mixture of compounds with the following composition, based on the results obtained by the University of Waterloo and from the vortex reactor at NREL.

<u>Compound</u>	<u>Molar Percent</u>	<u>Weight Percent</u>
hydroxyacetaldehyde	38%	33%
acetic acid	27%	23%
acetol	9.3%	9.8%
guaiacol	3.7%	6.6%
syringol	1.4%	3.3%
formic acid	7.5%	4.8%
coniferol	2.6%	6.6%
phenol	2.4%	3.3%
benzene	2.9%	3.3%
toluene	2.5%	3.3%
furfural	2.4%	3.3%

A three dimensional plotting program was used to graph the production of hydrogen by steam reforming as a function of temperature and the molar ratio of steam to carbon content (R). Figures 1, 2 and 3 show these plots for hydroxyacetaldehyde, syringol and the mixture of model compounds, respectively. These should be viewed as qualitative tools only and not for the determination of optimal operating parameters; the region to work within when designing experimental conditions can be approximated from the plots. It will not be possible to model the thermodynamics of the actual oil because of its complexity and limitations in the ASPEN Plus component data bank.

A more useful method of estimating experimental conditions is to define a practical operating temperature and calculate the yield of hydrogen as a function of R. Because pyrolysis oil vapors are produced at approximately 450°C to 600°C, thermodynamic simulations were performed at a reaction temperature of 500°C. Figures 4, 5 and 6 show the mole fraction of hydrogen in the product as a function of R at 500°C for hydroxyacetaldehyde, syringol and the mixture of compounds, respectively.

Figure 7 shows the approach of many of the model compounds and the mixture of compounds to maximum stoichiometric yields of hydrogen as a function of R. The most important result from this plot is that the necessary amount of steam is dependent only on the carbon content of the compound. Differences in the results between compounds can be attributed to the approximations made in the thermodynamic calculations. Therefore, given the carbon content of the pyrolysis oil, the appropriate amount of steam for high hydrogen yields can be estimated. Approximately 6.5 moles of steam per carbon are needed to achieve 80% of the stoichiometric maximum yield of H<sub>2</sub>. For 90% of the maximum, 9.0 - 9.5 moles of steam per carbon are required. This suggests that a wide range of combinations of operating variables is possible to obtain near stoichiometric yields. Simulation results are currently being used to design laboratory experiments.

# Hydroxyacetaldehyde Shift Conversion

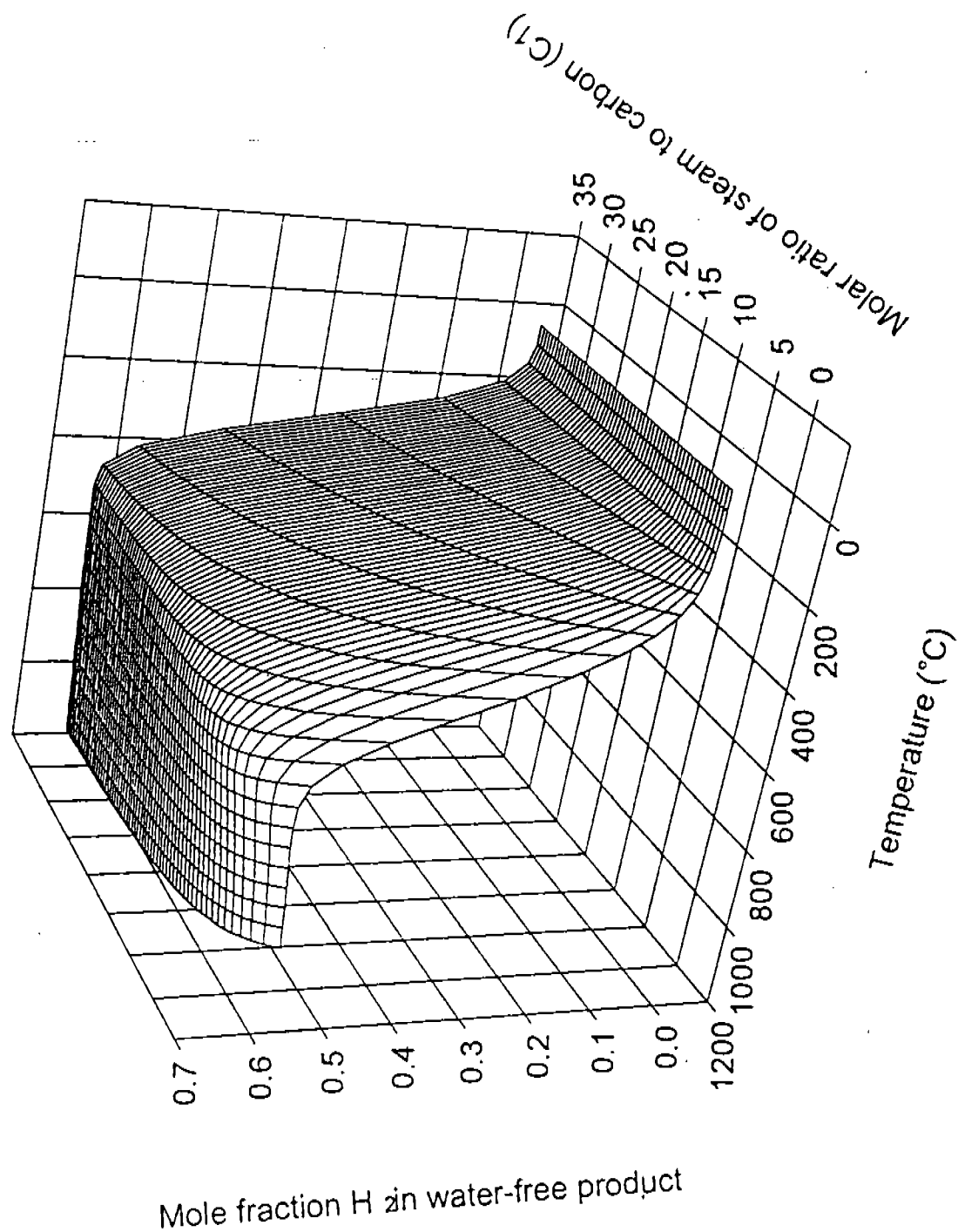
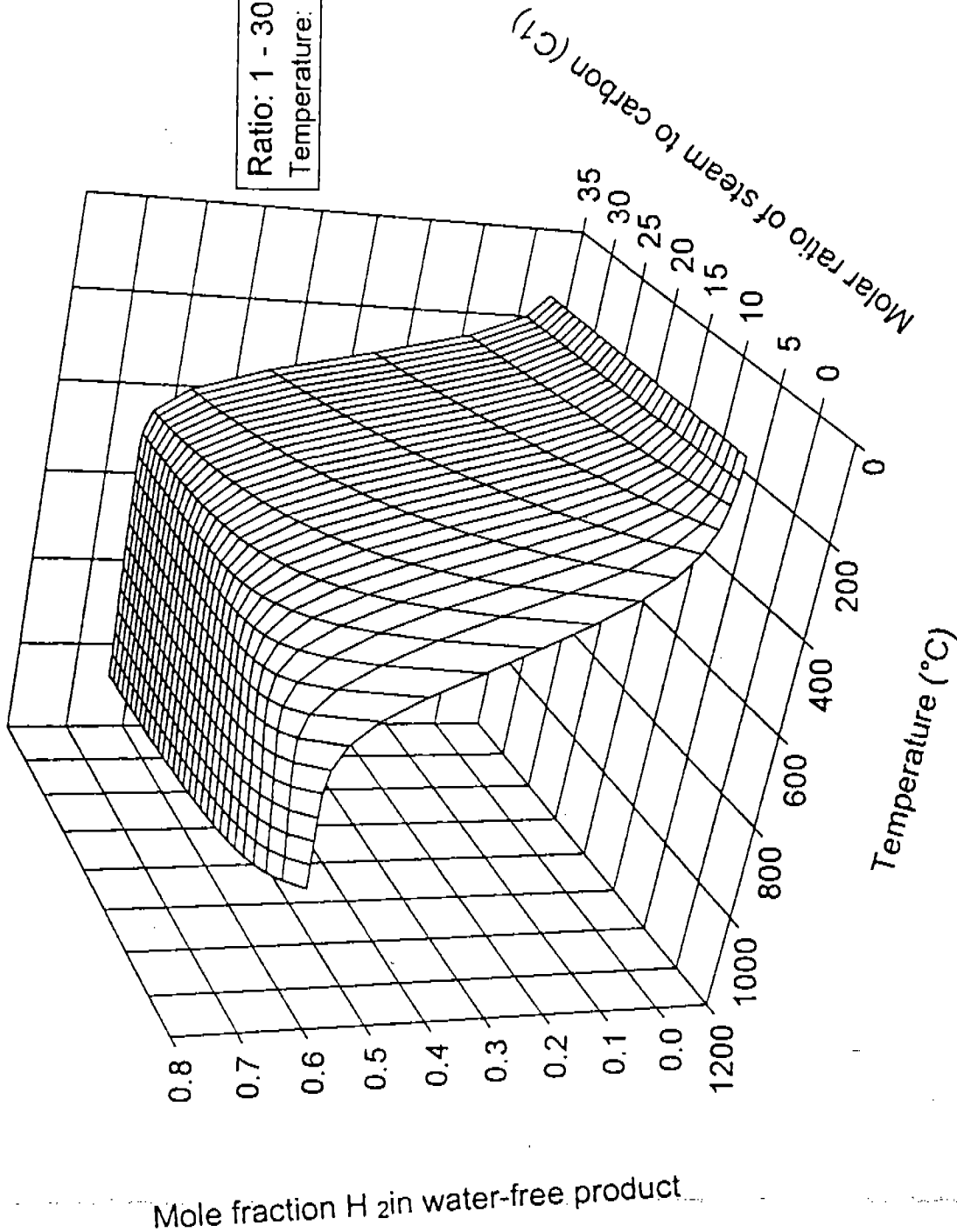


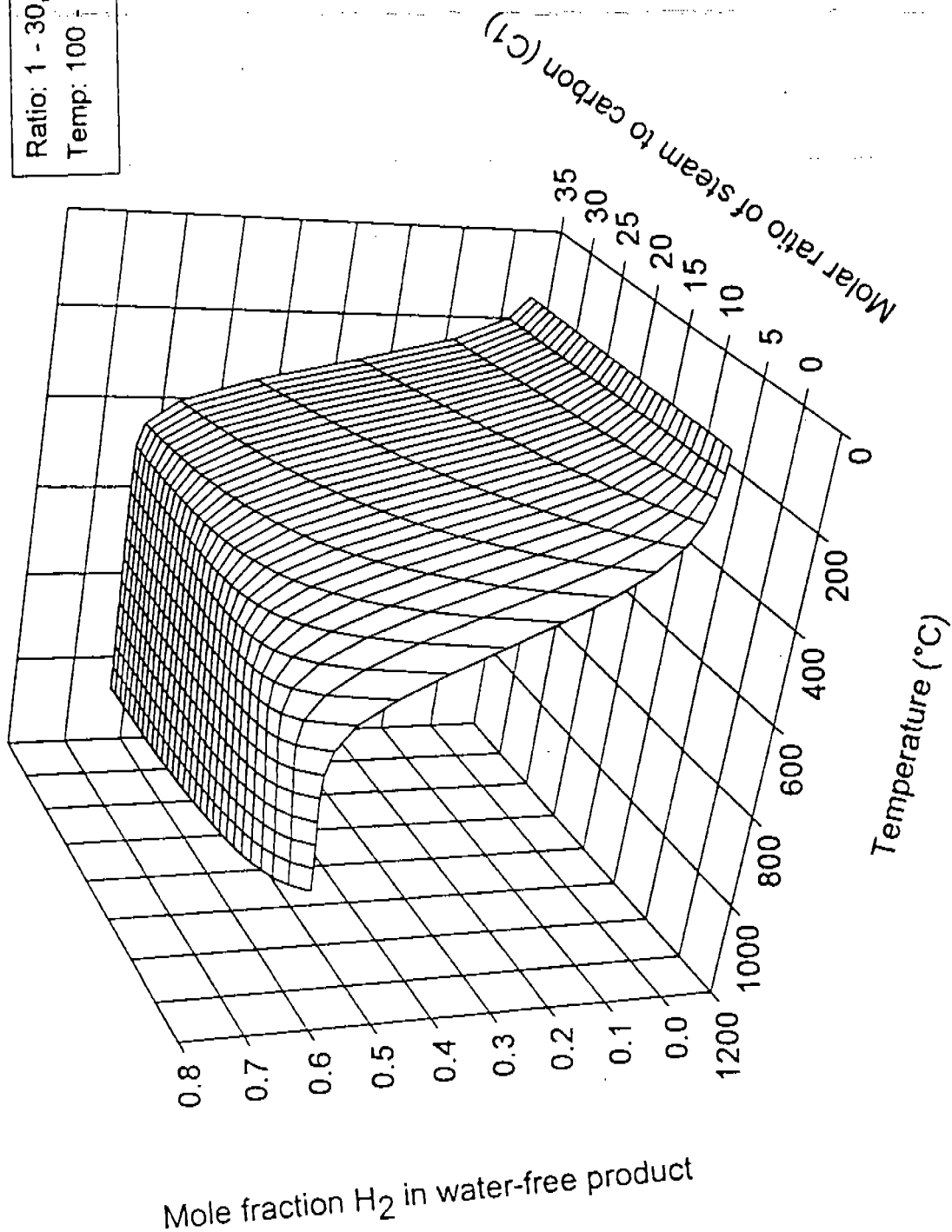
Figure 1

# Syringol Shift Conversion

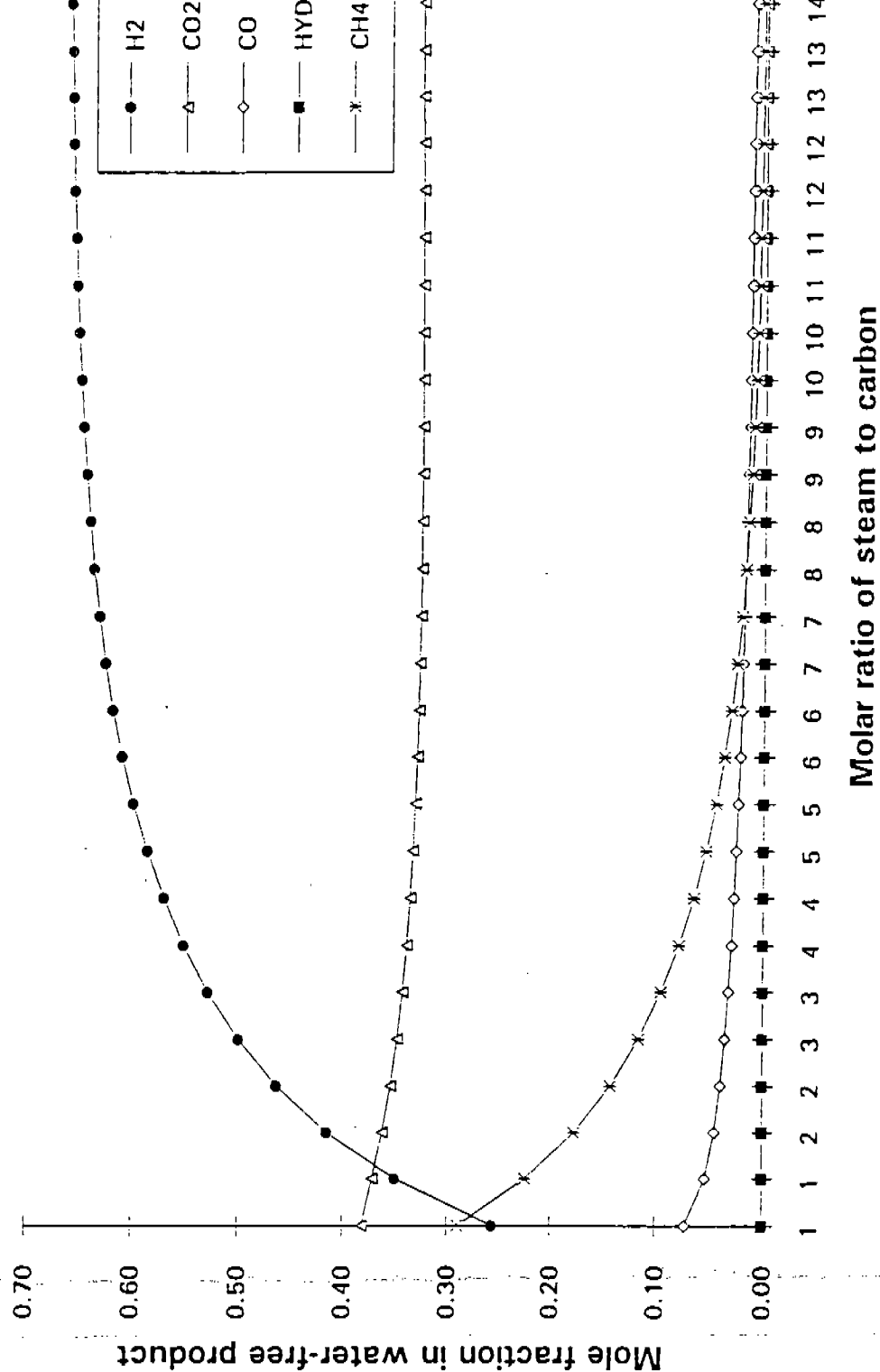


# Compound Mixture Shift Conversion

Ratio: 1 - 30, incr = 1  
Temp: 100 - 1000, incr = 50



# Hydroxyacetaldehyde Shift Conversion at 500 °C



# Syringol Shift Conversion at 500 °C

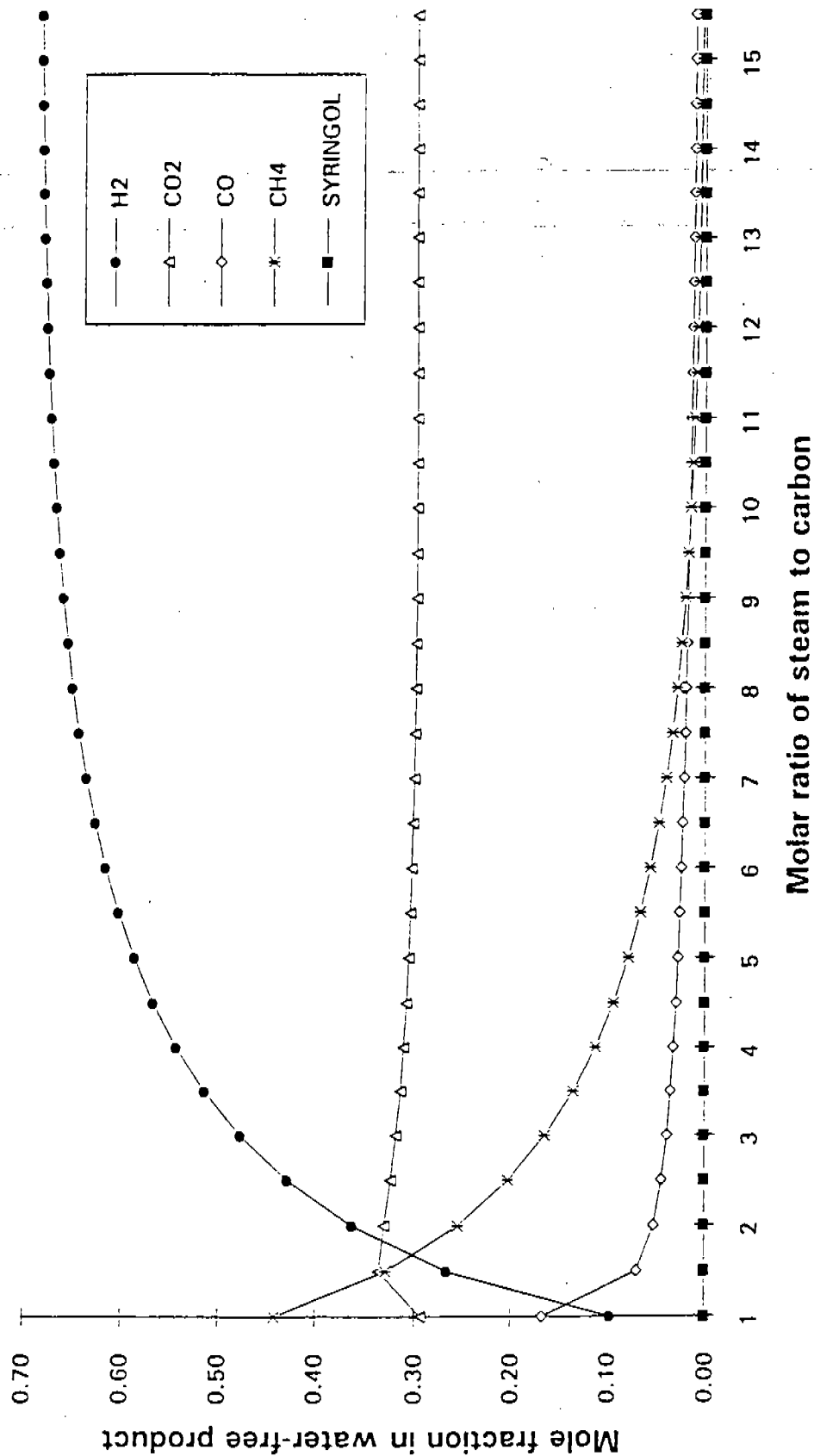
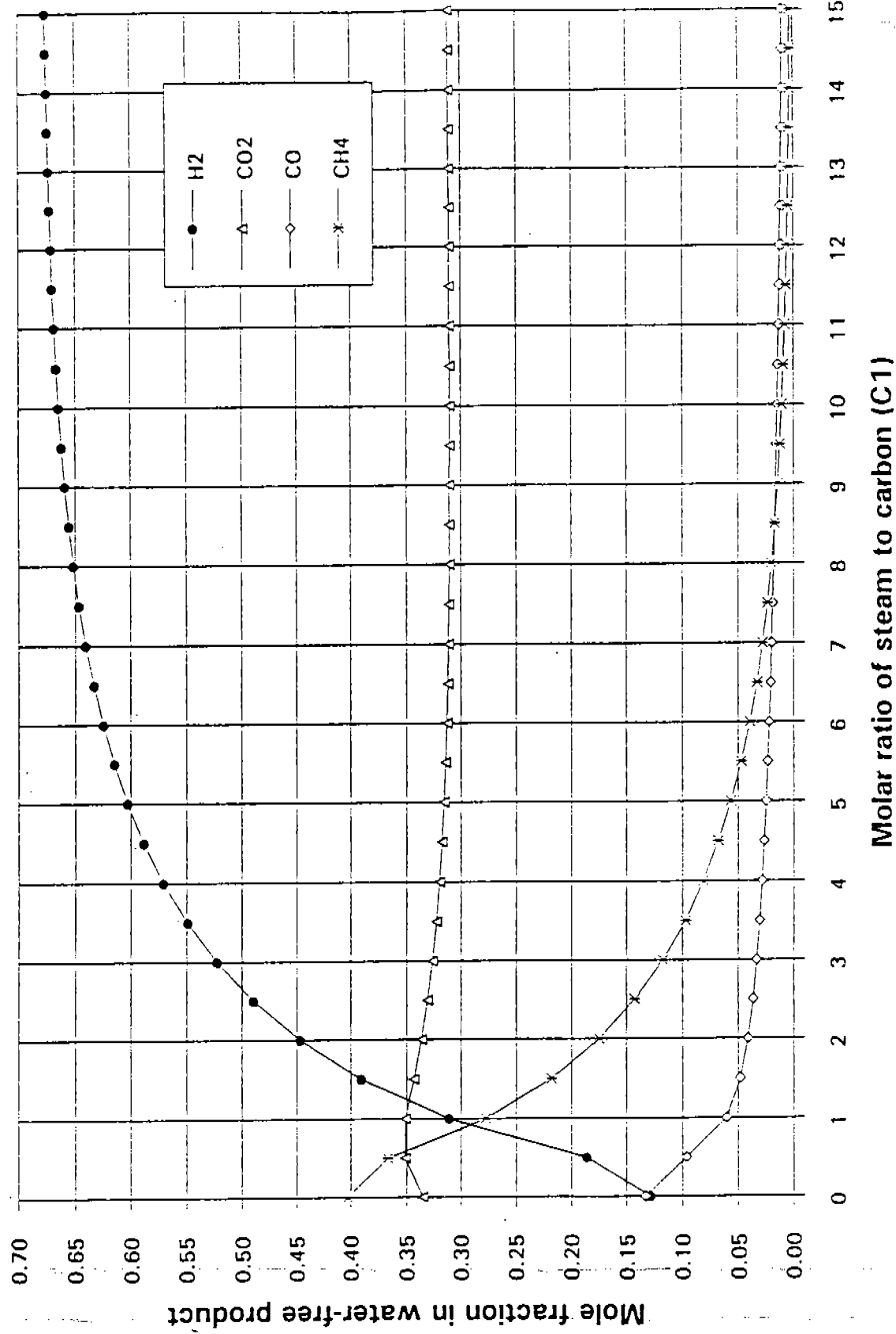


Figure 5

# Compound Mixture Shift Conversion at 500 C



# Approach to Maximum Stoichiometric Yield of Hydrogen at 500 °C

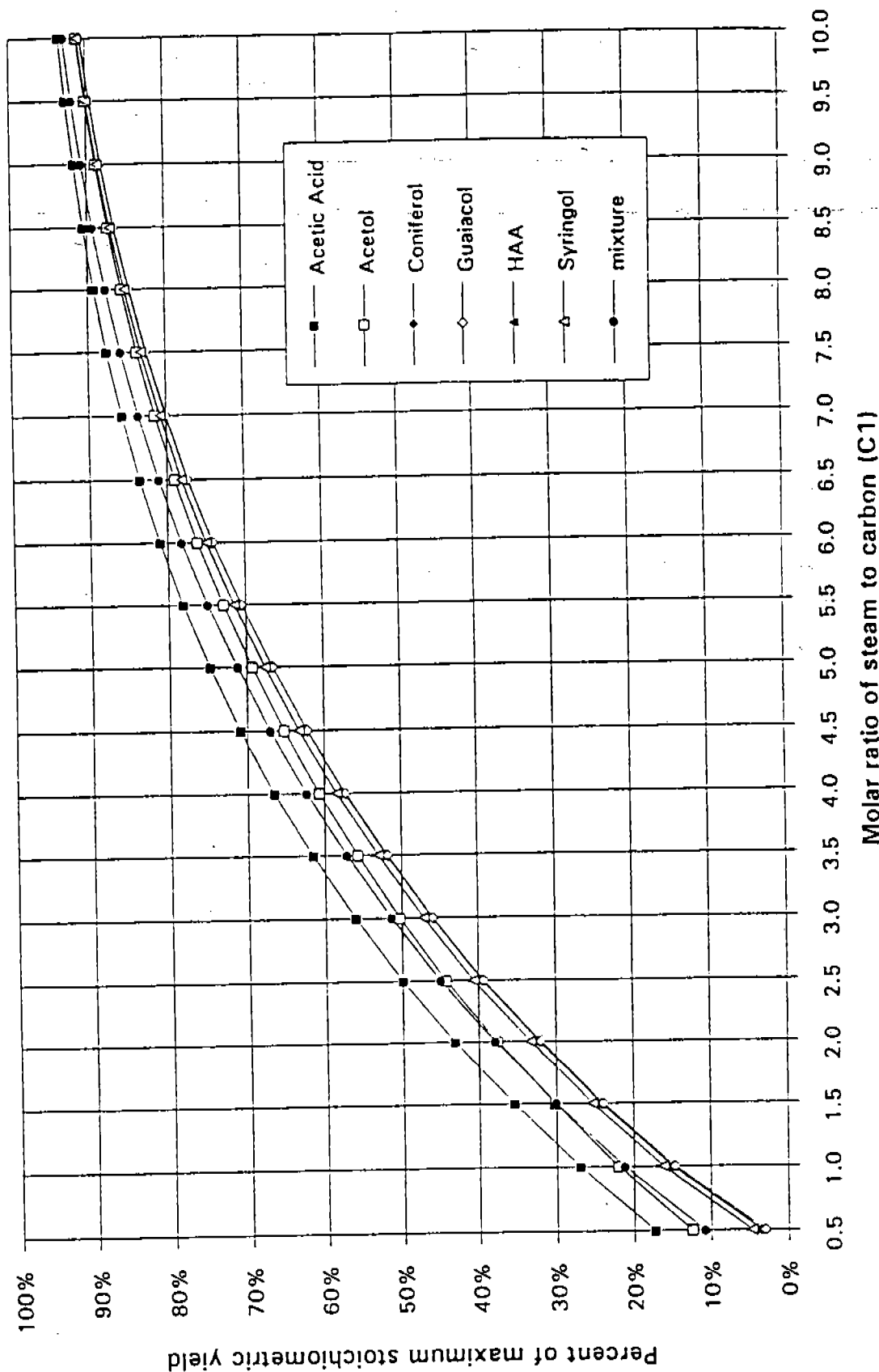
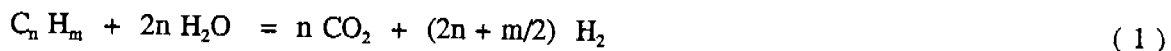
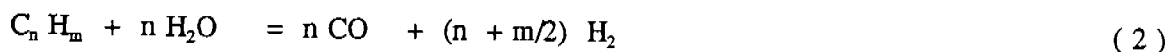


Figure 7

well known processes. When the objective is to maximize the production of  $H_2$  the stoichiometry describing the overall process is:



The simplicity of Equation 1 hides the fact that in a hydrocarbon reformer, the following reactions take place concurrently:



At normal operating conditions, reforming of higher hydrocarbons (Equation 2) is irreversible (Tottrup and Nielsen, 1982), whereas the methane reforming reaction (Equation 3) and the shift conversion reaction (Equation 4) approach equilibrium. A large molar ratio of steam to hydrocarbon will ensure that the equilibrium for reactions (3) and (4) is shifted towards  $H_2$  production.

The main problem in the steam reforming of hydrocarbons is carbon formation. Three types of carbon may be formed: whiskers, encapsulating deposits ("polymers"), and pyrolytic carbon (Rostrup-Nielsen and Tottrup, 1979). The carbon formation is related to the kinetics, and hence the selectivity, of the catalyst. In steam reforming, adsorption of hydrocarbons on the metal sites (Ni is commonly used) is followed by dehydrogenation and cracking. This results in smaller  $C_x H_y$  adsorbed fragments which can polymerize to unwanted intermediates and lead to coke formation. These reactions compete with reactions of the adsorbed water species. The catalyst must then be formulated to supply enough adsorbed  $H_2O$ -derived species, mainly OH and H, to overcome the coke formation reactions. This implies that the adsorbed OH and H must have sufficient surface mobility to reach the adsorbed hydrocarbon-derived species and react with them (Rostrup-Nielsen, 1984).

The steam adsorption capability can be significantly improved by promoting the classical Ni-alumina or Ni-silica/alumina formulations with Ca and/or K. An alternative is the use of magnesia as magnesium-aluminum spinel which enhances steam adsorption and can be prepared as high surface area refractory ceramic pellets.

The reforming operation requires relatively high steam/carbon molar ratios ( $S/C_1 = 3.5 - 5.0$  for methane), adequate temperature profiles in the tubular reactor (low inlet temperature increased along the tube length to a maximum of  $750^\circ C - 775^\circ C$  due to the structural constraints of the Ni-Cr alloys used), and a Ni-based catalyst (20-30 wt% as NiO) on a refractory support having appropriate steam adsorption characteristics as previously discussed. The reforming operation is not very sensitive to pressure which is essentially dictated by the applications of the product  $H_2$  (Patil, 1987). The NiO is reduced to its metal form prior to use. Space velocities used in tubular reformers are typically comprised between 1500-2000 (volume of  $C_1$  equivalent/h/volume of catalyst).

Sulfur is the most severe catalyst poison. Biomass-derived feedstocks, i.e. biocrudes, have only traces of sulfur and thus a desulfurization unit prior to the reformer may not be necessary. However, because of the oxygenated nature of the pyrolysis oil, the catalyst to be used in the reforming process must be able to handle high percentages of oxygen-containing functional groups. Efforts to modify steam reforming catalysts and render them less susceptible to poisoning by heteroatoms, mainly sulfur, have led to the development of novel preparations. Thus, sulfur resistant rare earth promoted catalysts for gas oil feeds have been available since the mid-eighties (Patil, 1987). The unreduced catalyst form is a mixture of NiO, rare earth oxides and  $Zr_2O_3$ . The applicability of this family of catalysts to reform oxygenates is not known. However, their satisfactory performance in the presence of sulfur makes such preparations attractive for the reforming of oxygen-containing molecules.

Aznar et al (1993), have clearly demonstrated that steam reforming syngas obtained from the gasification of lignocellulosics is possible using commercially available Ni-based catalysts (Topsoe R-67 and RKS-1), even with rapid deactivation of the catalyst after a few hours. Tars produced during gasification contain a high percentage of polycyclic aromatics, while pyrolysis oil is essentially a mixture of carbohydrate-derived fragments and lignin-derived phenolics (Elliott, 1988).

Literature on the steam reforming of oxygenates follows within two categories:

- Reforming methanol and ethanol
- Reforming oxygenated aromatics, i.e. cresols

Methanol reforming is of interest as a process for the production of  $H_2$  in numerous applications, hydrogenation of organic compounds and fuel cells being the most obvious. A large body of information has thus been accumulated on the catalytic reforming of methanol (the C1 alcohol). The comparison with methane, the analog  $C_1$  hydrocarbon, is thus appropriate. Methane requires high temperatures ( $> 500^\circ C$ ) to be effectively steam reformed. The mechanism has been proposed as follows (Ross et al, 1978):

- Methane, or any other hydrocarbon, is dissociatively adsorbed on the metal sites
- $H_2O$  is also dissociatively adsorbed on the Al sites, hydroxylating the surfaces
- Metal-catalyzed dehydrogenation takes place creating adsorbed hydrocarbon-derived fragments
- The OH surface groups migrate to the metal sites, activated by the temperature, and they eventually form intermediates leading to carbon oxides.

Methanol can be steam reformed at much lower temperatures ( $< 300^\circ C$ ) than methane. A variety of catalysts are capable of carrying out the conversion including reduced NiO-based preparations (Mizuno et al, 1986), reduced CuO/ZnO shift preparations (extensive literature cited by Amphlett et al, 1985; Su and Rei, 1991), Cu/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> (Takahashi et al, 1982), Cu/ZrO<sub>2</sub> (Takezawa et al, 1987), and Pd/ZnO (Iwasa et al, 1993). The product slate is markedly affected by the type of catalyst and the experimental conditions used. Two main mechanisms have been proposed (Jiang et al, 1993 a and 1993 b):

- The decomposition-shift mechanism where the chemisorbed methanol is totally

- The formate mechanism initially proposed by Takahashi et al (1982) is based on the formation of methylformate ester on the catalyst surface between two adsorbed species,  $\text{H}_3\text{CO}$  and  $\text{HCO}$ . The ester is hydrolyzed to methanol and formic acid. The latter decomposes directly to  $\text{CO}_2$  and  $\text{H}_2$  with 100% selectivity i.e. no CO is formed.

Ethanol reforming has been studied with two main objectives. Iwasa and Takezawa (1991) have reformed ethanol to study the formation of acetic acid. They have shown that acetaldehyde is the key intermediate when Cu-based catalysts are used. They found that the role of the support is important; Cu alone shows very high selectivity towards acetaldehyde (88% at  $250^\circ\text{C}$ ), whereas the presence of a support (either  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , or  $\text{ZnO}$ ) markedly affects this selectivity, producing a diversified number of intermediates at significant concentrations. Garcia and Laborde (1991) did a thermodynamic study on the reforming of ethanol to  $\text{H}_2$ . They concluded that  $\text{H}_2$  production requires higher temperatures than those needed for the reforming of methanol and that steam to ethanol ratios higher than 10 (equivalent steam to  $\text{C}_1$  ratios higher than 5) were required to prevent carbon formation.

Steam reforming of oxygenated aromatics has been directed towards the dealkylation of cresol. The reaction proceeds at temperatures of  $400^\circ\text{C}$ - $500^\circ\text{C}$  and steam to carbon ratios of 6 using Pd, Rh or Ni on alumina, silica or chromia-alumina. The predominant reaction is degradation to  $\text{H}_2$  and CO (Daly, 1980; Duprez, 1992). Assafi and Duprez (1988) proposed a mechanism in which the OH from the aromatic ring participates in the overall reaction process in the same manner as the OH group derived from the dissociation of water. Most important, under the conditions used, the aromatic ring is "cracked" and thus total reforming may be indeed feasible.

From the work on steam reforming of oxygenated aromatics, dehydroxylation proceeds at a significant rate to produce aromatic species on the catalyst surface. Thus, we ought to consider how these aromatic species can be steam reformed. Duprez (1992) discusses the work of a Russian group who reformed mixtures of aliphatic and aromatic hydrocarbons using a combination of Ni and V at  $850^\circ\text{C}$ . Work conducted at much lower temperatures,  $440^\circ\text{C}$ - $480^\circ\text{C}$ , and at steam to compound ratios lower than 10 (equivalent S/ $\text{C}_1$  ratio close to 1), with complex aromatics on Rh - V on alumina (Kim, 1976) and on Rh, Pt and Ni on alumina and silica (Delahay et al, 1985) showed that with methylnaphthalene as feed, partial degradation to CO and  $\text{H}_2$  takes place in competition with ring opening and dealkylation. Delahay and Duprez (1985) concluded that intermediate hydrogenation favors but is not a necessary prerequisite for ring opening.

In summary,

- Reforming of hydrocarbons ( $\text{C}_1$ - $\text{C}_8$ , naphtha and gas oils) is well understood and proceeds readily at steam to  $\text{C}_1$  ratios (S/ $\text{C}_1$ ) between 3.5 and 5.0, and temperatures up to  $775^\circ\text{C}$ .
- The most commonly used catalyst is Ni on alumina. Ca, K and Mg are often used with the alumina to enhance water adsorption, lower the acidity and favor mobility of the OH species on the surface.
- Alternate catalyst formulations have been developed to increase the resistance of the catalyst to poisoning, particularly by sulfur. These novel catalysts are also Ni-based with

mixtures of rare earth oxides and a refractory support.

- Methanol, a prototype of an oxygenated molecule, is readily steam reformed at low temperatures ( $< 300^{\circ}\text{C}$ ). Cu-based catalysts and recently developed Pd/ZnO preparations are extremely selective towards the formation of  $\text{CO}_2$  and  $\text{H}_2$  via the formate ester mechanism.
- Ethanol requires higher reforming temperatures than methanol to be reformed at appreciable rates. The mechanism proceeds through acetaldehyde and ethylacetate intermediates on the same Cu-based catalysts used for the methanol reforming.
- The existing data on oxygenated aromatic compounds, i.e. cresols, suggest that they can be steam reformed using known catalyst preparations. Little is known, however, about optimum experimental conditions that will result in long-term catalyst activity.

When considering the biocrude composition shown in Table 2, it is clear that challenges in catalytic steam reforming will be linked to the ability of the catalyst to handle the "pyrolytic lignin fraction" as well as the carbohydrate-derived fractions: monomeric sugars, anhydrosugars, and oligomers. Our goal is to find a catalyst formulation that can reform both the complex and simple molecules present in the biocrude while limiting undesirable side reactions which will lower the yields of  $\text{H}_2$ .

If the oxygen in the aldehydes, alcohols and acids could be removed as  $\text{CO}_2$ , via ester intermediates as in methanol reforming, the production of  $\text{H}_2$  would then be maximized. This could be done if, in the pyrolysis operation, a low molecular weight fraction of the biocrude is separated from a high molecular weight fraction during the condensation of the pyrolytic vapors. The low molecular weight fraction (a mixture of simpler compounds like hydroxyacetaldehyde, acetic acid, ethylene glycol, formaldehyde, glyoxal) could be reformed at low temperatures using the Cu-based or the Pd/ZnO catalysts.

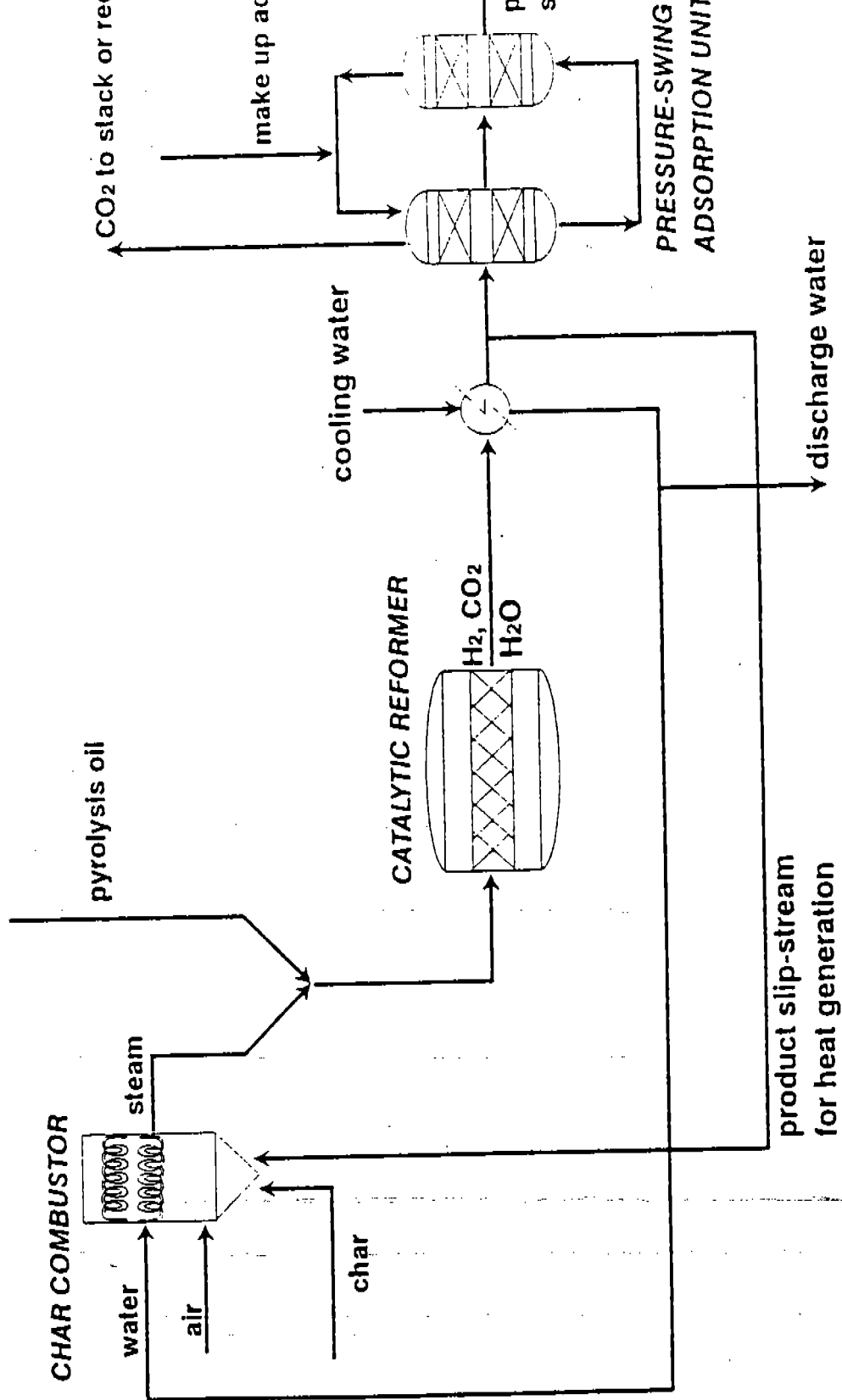
An alternate approach is to conduct the steam reforming of the entire biocrude near equilibrium conditions. By an appropriate choice of steam to biocrude ratio, temperature and residence time, the reforming could maximize the  $\text{H}_2$  production. This may be possible, according to the literature reviewed, by choosing stable and resistant Ni-based catalysts operating in the  $700^{\circ}\text{--}800^{\circ}\text{C}$  range. An appropriate temperature profile through the reactor will have to be developed experimentally to carefully control coke formation. A favored combination could be: NiO (20-30 wt%), MgO (10-15 wt%),  $\text{Al}_2\text{O}_3$  (50-65 wt%), rare earth oxides (5-15 wt%), and a promoter like  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ , or  $\text{WO}_3$  (5-10 wt%).

## Process Design

Two scenarios for the production of hydrogen from pyrolysis oil can be envisioned. One would involve a regionalized system of hydrogen production with small and medium-sized pyrolysis units providing biocrude to a centralized reforming unit. The alternative is to pyrolyze biomass in a large unit and feed the uncondensed vapors directly to the reforming unit. The first case has the advantage of the availability of cheaper feedstocks, perhaps biomass waste. In the integrated system, however, the costs of condensing the vapors to the oil and transporting them to the hydrogen facility are avoided.

A conceptual process design to make hydrogen from pyrolysis oil is shown in Figure 8. Unlike other

# Hydrogen From Pyrolysis Oil



reforming processes, this process involves very few unit operations, which should increase its economic feasibility. Because of the low sulfur content of biomass, a sulfur removal system is not likely to be required, while one is always used in petroleum and methane reforming. Also, according to thermodynamic simulations and current experimental results, only one medium temperature reformer is required; conventional methane reforming uses a furnace-like converter followed by a high temperature reformer and a low temperature reformer.

In the process being evaluated, pyrolysis oil or the uncondensed vapors are fed with steam into a catalytic reactor. Laboratory experiments will choose a suitable catalyst and reactor configuration; the base-case will use a fixed-bed catalytic reactor. The reaction will occur at 500°C, and the ratio of steam to oil will be determined by experimental results and economic optimization. Since the overall reaction of pyrolysis oil to  $H_2$  is endothermic, the char produced in the pyrolysis of the biomass will be burned to produce heat and steam. Preliminary energy balances indicate that a fraction of the oil may also be used as a source of heat, especially in the centralized reformer supplied by satellite pyrolysis units.

In the base-case design, a pressure swing adsorption unit will be used to purify the  $H_2$  produced. This was chosen because of commercially available processes such as the light hydrocarbon reforming process by Foster Wheeler USA, which is designed to purify 1 MM scfd to 95 MM scfd reformed gas. Alternative purification processes include extraction with monoethanolamine and membrane separation.

As information becomes available, the process will be simulated in ASPEN Plus. This will facilitate sensitivity runs and the implementation of process design changes. As an economic model is developed, results from process sensitivity runs will be incorporated into the cost of the project.

## Economics

Preliminary calculations were performed in order to determine the boundaries of economic feasibility of the process. To examine these boundaries before plant costs can be figured, the ratio of the current market selling price of  $H_2$  to the pyrolysis oil production cost was calculated. If the ratio is greater than one, the process has the potential to be economically feasible. This method assumes that the process to produce  $H_2$  is completely free of capital and operating costs. The results, therefore, set the minimum limits on the recovery of theoretical hydrogen and product selling price.

The maximum stoichiometric amount of  $H_2$  was calculated as that obtained by reforming all of the carbon in the oil with steam plus the hydrogen in the oil, where the oil was defined to have the formula  $CH_{1.33}O_{0.53}$ , as described earlier. The equilibrium amount was not used because of the difficulty in simulating the thermodynamics of pyrolysis oil reforming on ASPEN Plus. This is due to lack of reliable thermodynamic data and the complexity of the pyrolysis oil. The current selling price of  $H_2$  in industry is between \$5.00/MM Btu and \$15.00/MM Btu, depending on the size of the production facility.

For these calculations, the feedstock was considered pyrolysis oil rather than biomass, in order to take into account the cost of the pyrolysis process. The cost of the oil is \$0.141/kg, as calculated in an NREL report by C. Gregoire, on producing pyrolysis oil from biomass for power generation. This study used a biomass cost of \$2.50/MMBtu, which is equivalent to \$42/dry ton.

Tables 3 and 4 show the results of the preliminary economic calculations. Table 3 is the profitability ratio

wood feed (tons)	1000
wood feed (kg)	907,186
oil cost (\$/kg)	0.141
oil produced (kg)	589,671
oil cost (\$)	83,144
kg H <sub>2</sub> /kg oil	0.197
% recovery of stoichiometric maximum	70%

current selling price of H <sub>2</sub>		product price (\$)	product \$/feed \$ *
\$/MMBtu	\$/kg		
5.00	0.67	54,767	0.66
5.50	0.74	60,244	0.72
6.00	0.81	65,720	0.79
6.50	0.88	71,197	0.86
7.00	0.94	76,674	0.92
7.50	1.01	82,150	0.99
8.00	1.08	87,627	1.05
8.50	1.14	93,104	1.12
9.00	1.21	98,581	1.19
9.50	1.28	104,057	1.25
10.00	1.35	109,534	1.32
10.50	1.41	115,011	1.38
11.00	1.48	120,487	1.45
11.50	1.55	125,964	1.52
12.00	1.62	131,441	1.58
12.50	1.68	136,917	1.65
13.00	1.75	142,394	1.71
13.50	1.82	147,871	1.78
14.00	1.89	153,348	1.84
14.50	1.95	158,824	1.91
15.00	2.02	164,301	1.98

\*feed = pyrolysis oil  
inputs are in bold

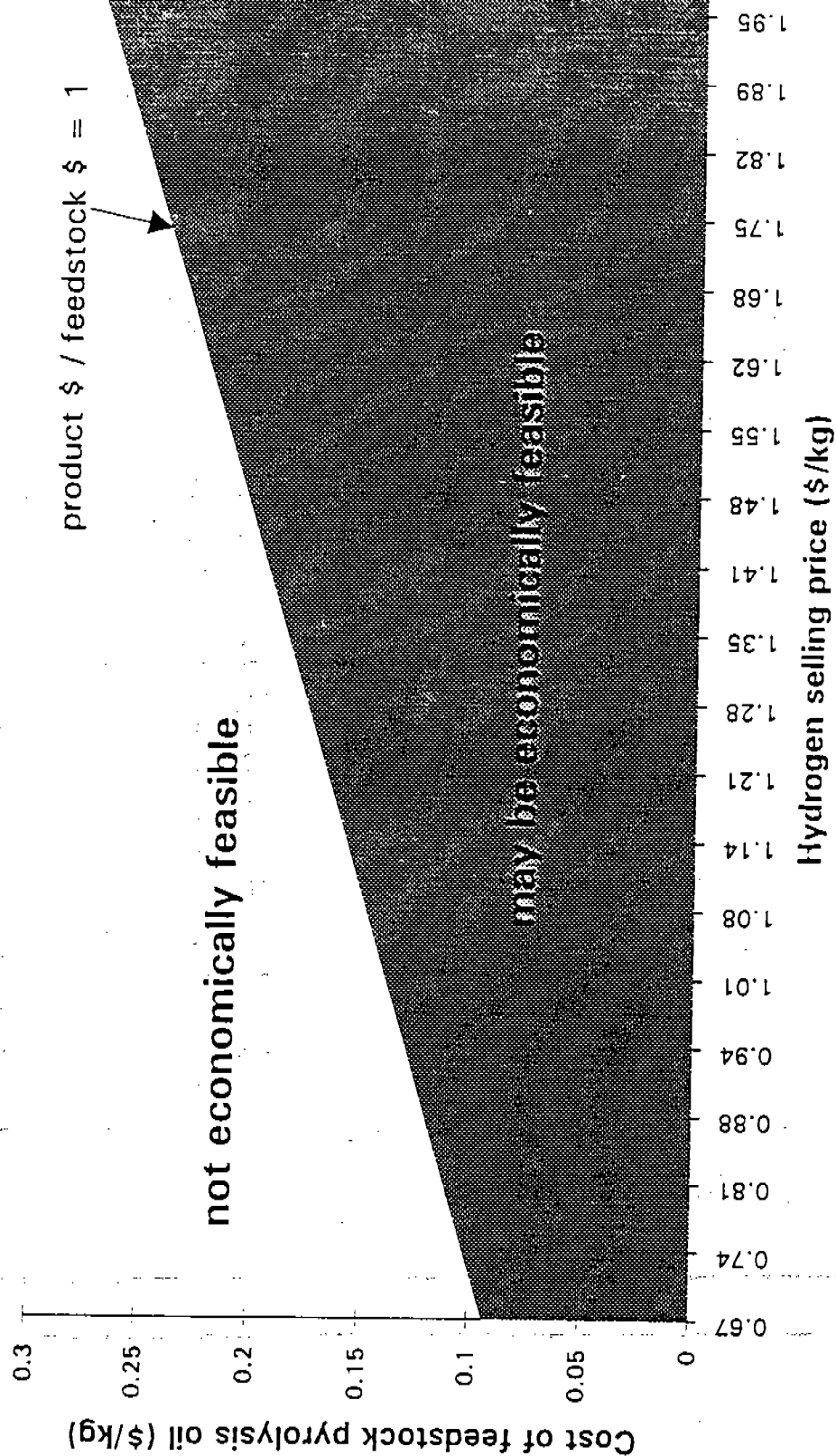
Table 4: Profitability vs. Percent Recovery of Stoichiometric Maximum  
(assumes a no-cost process for producing hydrogen)

H2 selling price (\$/MMBtu)	8.8
H2 selling price (\$/kg)	1.19
wood feed (tons)	1000
wood feed (kg)	907,186
oil cost (\$/kg)	0.141
oil produced (kg)	589,671
oil cost (\$)	83,144
kg H2/kg oil from reforming	0.197

% recovery	H2 produced (kg)	product price (\$)	product \$/feed \$ *
100%	116,165	137,700	1.66
95%	110,357	130,815	1.57
90%	104,549	123,930	1.49
85%	98,740	117,045	1.41
80%	92,932	110,160	1.32
75%	87,124	103,275	1.24
70%	81,316	96,390	1.16
65%	75,507	89,505	1.08
60%	69,699	82,620	0.99
55%	63,891	75,735	0.91
50%	58,083	68,850	0.83
45%	52,274	61,965	0.75
40%	46,466	55,080	0.66
35%	40,658	48,195	0.58
30%	34,850	41,310	0.50
25%	29,041	34,425	0.41
20%	23,233	27,540	0.33
15%	17,425	20,655	0.25
10%	11,617	13,770	0.17
5%	5,808	6,885	0.08
0%	0	0	0.00

\*feed = pyrolysis oil  
inputs are in bold

# Limit on Potential Economic Feasibility of Hydrogen from Pyrolysis Oil at 70% Stoichiometric Maximum



as a function of the selling price of  $H_2$ , assuming that 70% of the total hydrogen available in the process can be recovered. From Table 3, if 70% recovery can be achieved, the selling price of  $H_2$  must be at least \$7.50/MM Btu. Again, this does not take capital and operating costs into account.

Table 4 shows the profitability ratio as a function of the percentage recovery. For this table, calculations were made based on a  $H_2$  selling price of \$8.80/MM Btu, corresponding to a moderate size hydrogen facility of 10 MM scfd. Table 4 shows that if the selling price is \$8.80/MM Btu, 60% of the  $H_2$  that is available from reforming pyrolysis oil must be recovered to reclaim the cost of the feedstock; more would be necessary to cover capital and operating expenses.

Figure 9 shows the combinations of  $H_2$  selling price and feedstock cost that will result in a ratio greater than one. Hydrogen from pyrolysis oil has the potential to be economically feasible if costs fall within the shaded region. This graph assumes that 70% of the maximum stoichiometric  $H_2$  will be recovered. The pyrolysis oil cost will depend heavily on the cost of the biomass; a regionalized system to produce oil for a central hydrogen facility could utilize waste biomass which would bring down the cost of the oil considerably.

## Conclusions

Fast pyrolysis of biomass is an advanced technology to produce a biocrude in high yields (70-75 wt% of anhydrous biomass). This biocrude is a complex mixture of simple aldehydes, alcohols and acids together with more complex carbohydrate and lignin derived oligomeric materials. Fractional condensation of the pyrolytic vapors could separate the simple monomeric materials, which comprise about one third to one half of the biocrude from the complex oligomeric fraction. Steam reforming of the simple monomeric materials is thermodynamically and chemically feasible. By a proper choice of catalyst esters, intermediates could be favored, which would shift the selectivity to  $CO_2$  and  $H_2$ . Little or no CO will be then produced.

Steam reforming of the entire biocrude is thermodynamically feasible. High steam to carbon ratios relative to methane reforming, which requires ~5 moles of steam per mole of carbon, will be needed to ensure that the equilibrium shifts towards  $H_2$  from the analysis of the literature. Thermodynamically, this ratio is dependent on the carbon content of the compounds being reformed. Reforming the complex oxygenates seems chemically possible. The oxygenates rapidly dehydroxylate and aromatics are formed on the surface of the catalyst. Carbon-carbon bonds are then ruptured and a large supply of OH and H species ensure that carbon formation is minimized or even suppressed. This will require modifications of known reforming catalysts and specific temperature profiles which will be developed experimentally. Hydrogenation of the aromatics does not seem to be a prerequisite for low carbon production.

The fast pyrolysis technology options, i.e. fluid beds, entrained beds or ablative reactors, are at a level of advanced development; pilot and demonstration units are in operation and construction respectively. However, the steam reforming of a complex feedstock such as biocrude requires a major effort at the bench scale level to determine how catalysis can direct the surface chemistry towards gas forming pathways rather than undesirable carbon forming reactions, which will lead to coke formation. Modifications of existing catalytic preparations may be needed to reach this goal.

The strategy being studied consists of small- to medium-size regional fast pyrolysis units which will produce the biocrude from either dedicated crops or plantations, or will use waste lignocellulosics as feedstocks. The biocrude produced will be transported to a central reforming unit in a given region where  $H_2$  will be produced. Alternatively, if the biomass supply is abundant in a given region the fast pyrolysis and reforming operations can be conducted at the same site. Condensation of the vapors will not be necessary, giving a significant gain in efficiency. The biocrude is a more condensed form of energy than biomass, however. Thus, the choice between the two strategies will be based on transportation and feedstock costs.

The process concept is extremely simple: a desulfurization unit is not needed, and the biocrude can be atomized in a flow of steam which is then processed through a reforming unit. By a proper choice of conditions the near equilibrium design can be driven to maximize  $H_2$  production. A pressure swing adsorption unit will purify the gas stream.

The preliminary economics, based on input/output calculations (no plant or operating costs considered), with a price of biocrude of \$0.141/kg, suggest that the  $H_2$  cost, at 70% of the maximum stoichiometric yield from biocrude, will be \$7.50/MM Btu. Alternatively, if the  $H_2$  can be sold for \$8.80/MMBtu, at least 65% of the maximum must be recovered. A wide margin thus exists in which to include capital and operating costs and still make hydrogen from biomass pyrolysis economically attractive.

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